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(21) International Application Number: PCT/US97/06323 (22) International Filing Date: 15 April 1997 (15.04.97) (30) Priority Data: 60/027,323 2 October 1996 (02.10.96) US (71) Applicant: W.L. GORE & ASSOCIATES, INC. [US/US]; 551 Paper Mill Road, P.O. Box 9206, Newark, DE 19714 (US). (72) Inventors: LAXMINARAYAN, Anand; 109 Pegasus Court, Bear, DE 19701 (US). HENN, Robert, Lyon; 2640 Longwood Drive, Wilmington, DE 19810 (US). (74) Agents: CAMPBELL, John, S. et al.; W.L. Gore & Associates, Inc., 551 Paper Mill Road, P.O. Box 9206, Newark, DE 19714-9206 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: CO-CONTINUOUS POROUS STRUCTURES OF A COMBINATION OF POLYMERS (57) Abstract <p>Two (or more) continuous porous polymeric matrices are employed, one of which is microporous, in which the polymers matrices interpenetrate the porous areas of the other. Thus, the invention is a composite membrane made from two polymers. Thus, a composite of strong interpenetrating matrices is formed which exhibits properties of both polymers. For example, one polymer can impart strength, the other polymer improved radiation resistance, or one polymer can impart strength and the other improved reflectance of light.</p> <div data-bbox="690 1134 1356 1407"><p>PORE ePTFE</p><p>LOAD SOLUTION OF POLYMER 2</p></div>		

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TITLE OF THE INVENTION

CO-CONTINUOUS POROUS STRUCTURES OF A COMBINATION OF POLYMERS

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CROSS REFERENCE TO RELATED APPLICATIONS

This application is based on Provisional application Serial No.
60/027,323, filed October 2, 1996.

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FIELD OF THE INVENTION

This invention relates to porous polymers, and more specifically to a
combination employing at least one microporous polymer.

15

BACKGROUND OF THE INVENTION

Microporous polymers are used commercially in a wide variety of
applications. There are several attributes of microporous polymers that are of
interest for commercial use. These include among others, degree of porosity,
smallness of pore size, total surface area, and so on. The various attributes
that lend commercial significance to microporous polymeric products are
strongly dependent on the nature of the polymer used and on the
microstructure of the product. The type of product and the microstructure
desired in turn influence the choice of technique that is to be used to form the
microporous product and vice versa. Phase separation (also known as phase
inversion) of a polymer solution is one of the major techniques used to make
commercial membranes. This technique results in the formation of a monolithic
microporous polymeric product consisting of a single rigid continuous polymeric
(this may be a homopolymer, co-polymer or even blends of polymers) phase
that forms the back bone (or matrix) of the microporous product. The shape of
the polymeric matrix determines the microporous structure. The empty spaces
within the rigid polymeric matrix form the pores of the microporous product.

Phase separation techniques for the formation of polymeric microporous
structures have long been in existence. Phase separation is a process by
which an initially homogeneous polymer solution is caused to separate into a
polymer-rich phase and a solvent-rich phase. The polymer-rich phase upon
solidification forms the back bone of the microporous structure while the empty

spaces left behind, upon the extraction of the solvent-rich phase, forms the pores of the membrane. Phase separation occurs when the thermodynamic state of a system is altered by changing one of the system variables such as temperature, pressure or composition. Two of the common variables that are used to induce phase separation are temperature and composition. When variation in temperature is used to induce phase separation it is referred to as Thermally Induced Phase Separation (TIPS). When a non-solvent is used to vary the composition of an initially homogeneous solution and thereby induce phase separation it is called a Non-solvent Induced Phase Separation Process (NIPS). Composition may also be varied by allowing the solvent to evaporate. When this technique is used to form a microporous product it is called the dry phase separation process. These techniques have been used to form microporous products from polymers such as polypropylene, polyvinylidene fluoride (PVDF), polyethylene, and many others. Virtually any polymer that can be dissolved in a solvent can be processed into a microporous product by the TIPS, NIPS and dry phase separation techniques.

Microporous polymers can also be made by other techniques such as salt leaching or stretching. For example, microporous polytetrafluoroethylene can be made by expansion of PTFE extruded film according to Gore U.S.P. 3,953,566.

As pointed out above, microporous materials find use in a wide variety of applications. The performance of a microporous material and its applicability in any given application in the field depends on a variety of characteristics. These include mechanical properties, pore characteristics and surface/wettability characteristics. These characteristics are determined by the polymer used and the technique used to form the microporous product. Often the appropriate combination of mechanical properties, optical properties and pore structure are not possible within a monolithic microporous product made from a single polymer.

One of the ways of solving this problem is by making two or more microporous membranes from different materials and/or having different pore structures in order to take advantage of both polymer properties or different pore structures. For example, asymmetric membranes for gas separation have been prepared by layering a microporous and dense film membranes one on top of the other. Layering of two microporous structures have also been done in the past to get a gradation in pore sizes or to take advantage of the physical properties of two different polymers.

U.S. Patent 4,761,232 to Bright describes a macroporous polyethylene substrate which defines a network of interconnected macropores. The macropores are completely filled with a microporous matrix of polyvinyl chloride (PVC). The purpose is to protect the microporous PVC and thereby provide a more robust construction. The macropores are spaces between sintered grains of the polyethylene. The microporous structure is encompassed by the walls of the macropores. Therefore, the structure is not a structure where two polymers form a continuum by interpenetration of the void spaces of one another. Rather, the microporous PVC material forms inside the macropores of the polyethylene. Thus, there is no intertwining of polymers, as the pore size is determined solely by the pore size of the microporous material. In the Bright patent, the sole function of the macroporous material is as a strength support for the more fragile microporous PVC. Further Bright teaches that in order to have effective interconnectivity in the composite product the pore size of the macroporous support should be at least three times (and preferably ten times) the pore size of the microporous PVC.

SUMMARY OF THE INVENTION

In contrast, in this invention, two polymers co-act to provide and impart mutually advantageous properties to the resulting composite.

In the present invention, two continuous porous polymeric matrixes are used, at least one of which is a microporous network, in which the polymers matrices interpenetrate the porous void areas of the other. Thus, the invention is a composite membrane made from at least two intertwined polymers. Preferably both polymers will be microporous.

Contrary to the concept of layering membranes of two different polymers over one another, the composition of this invention does not consist of layered structures. In the current invention a structure of one polymer is formed in-situ around the porous structure of another porous polymer, which is referred to herein as the "base" polymer. When the pores of this base polymer interconnect, as they do in this invention, the resulting product is a co-continuous porous structure of two polymers either one of which would be capable of forming a porous network by itself.

Thus, the invention is a composition comprising interpenetrating matrixes of two polymers wherein each polymer has a structure consisting of a convoluted matrix so as to define convoluted, tortuous, interconnected void paths at least one such polymer having microporous size void paths throughout

said structure, and wherein said convoluted matrixes of each polymer interpenetrate the void paths of one another.

BRIEF DESCRIPTION OF THE DRAWINGS

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The foregoing summary, as well as the following detailed description of a preferred embodiment of the invention, will be better understood when read in conjunction with the appended drawings. In the drawings:

10 Figure 1 is a pictorial depiction of the preparation steps in preparing typical co-continuous microporous structures.

Figures 2a and 2b are pictorial depictions of a typical co-continuous microporous structures.

15 Figures 3a and 3b are SEMs of the surface of a co-continuous microporous structure of polystyrene and ePTFE (expanded PTFE) taken at 2 magnifications.

Figure 4 compares the % Reflectance of an ePTFE membrane to that of an ePTFE / Polystyrene composite at different wavelengths

Figure 5 is a micrograph of the cross-section of a co-continuous microporous structure of ePTFE and polystyrene.

20 Figure 6 is a SEM of the cross-section of a co-continuous microporous structure of low density polyethylene and ePTFE.

Figure 7a and 7b are SEMs of the cross-section of a co-continuous microporous structure of a thermoplastic polyurethane and ePTFE taken at 2 magnifications.

25 Figure 8a and 7b are SEMs of the cross-section of a co-continuous microporous structure of a thermoplastic polyurethane and ePTFE taken at 2 magnifications.

Figure 9 is a SEM of the cross-section of a co-continuous microporous structure of polypropylene and ePTFE.

30 Figure 10 is a SEM of the cross-section of a co-continuous microporous structure of high density polyethylene and ePTFE.

Figure 11a and 11b are SEMs of the surface of a co-continuous microporous structure of polyvinylidene fluoride and ePTFE taken at 2 magnifications.

35

DETAILED DESCRIPTION OF THE INVENTION

The porous structures are characterized by the substantially co-continuous nature of the two polymers. The structures are achieved by forming a porous structure of Polymer 2 within and around a pre-formed microporous structure of base Polymer 1. The porous structure of Polymer 2 is formed through conventional solution phase separation techniques such as the NIPS and the TIPS procedures described above. Such combinations of porous and microporous structures of two or more polymers may be used to alter and improve mechanical, surface, and transport properties of the microporous structure of the base polymer. Alternately, the combinations may be used to make porous structures with specific property requirements. To illustrate the concept by reference to specific polymers, base Polymer 1 can be expanded microporous polytetrafluoroethylene (ePTFE). Polymer 2 can be any one of a variety of polymers that can be dissolved in a solvent and loaded into the micropores of the ePTFE. In a preferred embodiment, Polymer 2 is also microporous and formed by interpenetrating the pores of the ePTFE microporous membrane.

The following is a brief description of the general process by which microporous membranes are made by the phase inversion/separation process. First, a solution of the polymer is made in a suitable solvent. Then the solution is cast into a desired shape. The solution is caused to phase separate into polymer-rich and solvent-rich phases. The type of phase separation employed (liquid-liquid phase separation or polymer crystallization) determines the microstructure. The polymer-rich matrix forms the solid or backbone structure of the membrane. The solvent-rich phase when extracted leaves behind empty spaces that form the pores of the membrane.

The general procedure for the formation of the co-continuous porous structures of this invention, where Polymer 1 is described in terms of the preferred Polymer 1, namely expanded porous PTFE, is as follows (referring to Figure 1).

1. A solution of the desired Polymer 2 is made in a suitable solvent. The preparation of the solution depends on the technique to be used to induce phase separation. In the TIPS process phase separation is induced by a drop in temperature. Consequently the initial solution is usually prepared at an elevated temperature. In the NIPS process phase separation is induced by the introduction of a non-solvent (which changes composition). In the dry phase separation process the solvent is allowed to evaporate causing loss in solvating

power and thereby inducing phase separation. The process temperature in any of the cases depends on the polymer and the diluent.

2. A microporous expanded PTFE membrane is employed. It is shown in Figure 1a where the cross-hatching depicts the pore walls and the space between represents the pores. The Polymer 2 solution is then loaded into the pores of the microporous membrane. This is shown in Figure 1b. In some cases the solvent spontaneously wets ePTFE and takes the polymer with it into the pores (void volume) of the membrane. In other cases the solution may have to be forced into the membrane. The technique used to force the polymer solution into the membrane depends on the amount of force required which in turn depends a variety of factors including the surface tension of the polymer solution, the molecular weight of Polymer 2, and pore size of the ePTFE membrane. The surface tension of the polymer solution determines its resistance to spontaneously wetting the membrane while the polymer molecular weight of the polymer will influence the viscosity of the polymer solution. A spontaneously wetting solution can be simply poured on to the membrane while a non wetting solution will have to be forced or drawn into the membrane. The smaller the pore size of the ePTFE membrane the greater will be the force required to impregnate the pores with the polymer solution. In some cases the solution can be forced into the membrane by hand using the bottom of an Erlenmeyer flask or a beaker. If the polymer solution is at a high temperature then the bottom of the Erlenmeyer flask or the beaker may have to be heated to the same high temperature. In other cases greater force may be required which may be attained using a carver press or vacuum.
3. The polymer solution is caused to phase separate. This step primarily controls the final microstructure of Polymer 2 within the ePTFE base Polymer 1. The method used to induce phase separation depends on the technique used. If the TIPS technique is being used then the ePTFE membrane loaded with the polymer solution is quenched to a lower temperature. The final microstructure of Polymer 2 using a given polymer is controlled by the type of phase separation that occurs. In the TIPS process the type of phase separation depends on the initial polymer concentration, the nature and type of the polymer and solvent, the temperature to which the ePTFE loaded with the polymer solution have been quenched to, and the rate at which it has been quenched. If the NIPS technique is to be used, the ePTFE loaded with the polymer solution is quenched into a non-solvent bath (non-solvent for the polymer but solvent for the diluent that is used to make the initially homogeneous polymer solution). Once again, the final microstructure

using a given polymer depends on the type of phase separation that occurs. In the NIPS process the type of phase separation in turn depends on the nature and type of polymer and solvent, initial polymer concentration and the composition of the casting solution. The different types of phase separation that can occur are liquid-liquid phase separation, solid-liquid phase separation or liquid-solid phase separation. The microstructure developed from each type of phase separation can be distinctly different. Within each type of phase separation mechanism, there are a range of structures possible. The different types of phase separations possible and the different microstructures possible are well documented in the literature (For e.g A. J. Castro U.S.P 4,247,498, D.R. Lloyd and J.W. Barlow AIChE Symposium Series 261 (1988) 28; D.R. Lloyd et al, Journal of Membrane Science 64 (1991) 1-53; J.G. Wijmans and C.A. Smolders in Synthetic Membranes: Science, Engineering and Applications, Eds. P.M. Bungy, H.K. Lonsdale and M.N. dePinho NATO ASI Series; Series C, vol. 81, 39-56). Figures 1c and 1d show two types of structures possible upon liquid-liquid phase separation of the Polymer 2 solution. In one, depicted by Figure 1c, it is seen that upon phase separation, Polymer 2 forms an intertwining polymer rich phase denoted by the heavy black lines, while the solvent rich phase is interspersed throughout the remaining pore volume (denoted by the lighter horizontally disposed lines). Upon extraction of solvent and drying, the intertwined structure shown in Figure 2a is obtained, where the heavy black portions denote the nodes and fibrils of an expanded microporous ePTFE Polymer 1; while the shaded lines denote the intertwined structure of Polymer 2.

In the other, depicted in Figure 1d, it is seen that upon phase separation, the polymer rich areas, denoted by the heavier black areas, tend to surround solvent rich phases which are the areas inside the circles of Figure 1d. Upon extraction of solvent from the Figure 1d structure, the structure of Figure 2b is obtained. Thus, a number of microstructures is possible using Polymer 2. This combined with another large number of microstructures for Polymer 1 yields a large variety of co-microporous structures possible from a single Polymer 1/Polymer 2 combination.

4. When the polymer-rich phase has solidified, the solvent-rich phase formed upon phase separation is extracted.

The extraction is usually carried out with a low boiling common solvent such as acetone, methanol, etc. The extraction is carried out by dipping the ePTFE membrane which now has the phase separated microstructure of Polymer 2 within it into the extractant bath.

5. The final membrane is dried (usually air drying followed by vacuum drying). The extractant is usually removed by drying.

6. The above results in a composite membrane that has two co-continuous polymer matrices; one of which is the PTFE and the other Polymer 2. The effective composite structure will depend upon the various factors including the initial concentration of polymer 2 in the solution, and the type of phase separation. Figure 2 gives a pictorial depiction of two possible co-continuous microporous structures.

The ratio of the amount of Polymers 1 and 2 is determined by two factors. These are the density of the ePTFE membrane and the starting concentration of Polymer 2 in the solution. The concept behind the invention is similar in some ways to that of the concept behind polymer blends. The properties of two different porous products are merged to form a composite porous product where the two porous structures rather than being layered over one another are intertwined with one another. By doing so, it is possible to manipulate and tailor the properties of porous products. These include surface characteristics, mechanical characteristics, optical characteristics and transport characteristics. Each of these characteristics could be influenced by the manipulation of structure and by the nature of the polymer. The addition of a second porous structure introduces additional degrees of freedom in controlling membrane properties. Polymer 2 may be any polymer which can be dissolved in a suitable solvent. The type of polymer may depend upon the final properties desired of the composite membrane. For example, if it is desired to improve the reflectance of the ePTFE membrane a polymer with a high refractive index would be suitable as the second polymer. On the other hand if improving the radiation stability of ePTFE is desired then a radiation stable polymer such as polyvinylidene fluoride (PVDF) or low density polyethylene may be the desired polymer. Representative of the base polymer as well as of Polymer 2 are selected from polyolefins, polystyrene, fluoropolymers, polyurethanes, polysulfones, polyamides, polyimides, polyacrylics, polyketones, polycarbonates, polyesters, rubbers, and co-polymers and blends thereof.

Examples of the influence of Polymer 2 on wetting characteristics and demonstrated by the fact that cyclohexanol will not spontaneously wet a 7 micron pore size expanded ePTFE membrane. However, a drop of cyclohexanol placed on a co-mps of ePTFE and polystyrene will spontaneously wet the membrane.

Water will not spontaneously wet ePTFE. However, a co-mps of a 7 micron (Mean Flow Pore Size) ePTFE and a hydrophilic thermoplastic polyurethane will spontaneously wet the membrane (See Example 4).

5 Examples of the influence of Polymer 2 on optical properties are shown in that the reflectance of light at different wavelengths by the ePTFE membrane can be increased by forming a co-mps of polystyrene and ePTFE (Figure 3) - (See Example 1) .

10 Examples of influence of Polymer 2 on mechanical properties are shown in that when ePTFE is subjected to radiation it loses its mechanical strength. It has been found that incorporating a microporous structure of low density polyethylene (LDPE) in the ePTFE improves the strength of the membrane after radiation (See Example 3).

15 Polystyrene is an inherently brittle material. It is be difficult to make a polystyrene membrane by itself that is mechanically strong. However, the co-mps of polystyrene and ePTFE is a easily handleable product.

Without intending to limit the scope of the present invention, the apparatus and method of production of the present invention may be better understood by referring to the following examples:

20 Test Procedures:

Mean Flow Pore sizes were determined using a Coulter Porometer I instrument as described in ASTM F 316-86.

25 Maximum pore sizes were determined either using the Coulter Porometer as described in ASTM F 316-86.

30 Air flows were determined using a Gurley Precision Instrument made by Teldyne Gurley (Model No. 4110). Gurley value as specified in this document is the amount of time required for 100cc of air to pass through a membrane under a pressure of 4.89 inches' of water through an orifice of 1.0 square inch area.

35 Water Entry Pressures (WEP's) were determined as the pressure required to cause water breakthrough. Water breakthrough is the minimum pressure required to intrude water through the largest opening of a dry hydrophobic membrane. The test rig for the measurement of WEP consisted of a base that has a bore of 1.5 cm in diameter and 10 cm height. This bore is filled with water. The membrane sample is placed across the 1.5 cm opening. A support plate is placed on the sample. The support plate is transparent and has a small bore of 1.5mm. A piece of pH paper is place between the support

plate and the membrane sample. The support plate is firmly clamped to the base. The water in the bore is pressurized using compressed air and the pressure at which the water leaks through the membrane and there is consequently a change in the color of the pH paper is the WEP.

- 5 Diffused reflectance was determined using a Perkin Elmer Lambda 18 spectrophotometer.

Example 1:

- 10 Polystyrene (MW 250,000, Cat# 18,242-7 from Aldrich Chemical Co.) was blended with cyclohexane (Aldrich Chemical Co.) in an Erlenmeyer flask at approximately 60°C, until a clear solution of 3 wt. % polymer was obtained. The Erlenmeyer flask was transferred to an oven maintained at 60°C. An expanded microporous PTFE (Mean Flow Pore size 1.46 +/- 0.65um, Maximum Pore Size 5.22 +/- 0.65 um) laminate was fixed onto a hoop. The hoop with the membrane in it was placed in the oven. The polystyrene solution was
15 poured onto the hoop. The membrane was readily wetted by the solution. The entire hoop was quenched into liquid nitrogen. The membrane was then immediately quenched into a bath of isopropanol at room temperature to extract the cyclohexane. The membrane was then dried by vacuum drying to
20 remove the isopropanol, resulting in a co-continuous microporous structure of polystyrene and PTFE (see Figures 3a and 3b which are SEMs taken at 0.20 kx. and 0.50 kx.

- Air flow of base ePTFE membrane = 0.8 sec (Gurley value)
 Air flow of Polystyrene/ePTFE composite = 1.5 sec (Gurley value)
25 WEP (Water Entry Pressure) of base laminate : 9.67 +/- 0.24 psi
 WEP of Polystyrene/ePTFE composite = 10.5 +/- 0.441psi
 Mean Flow Pore size of base laminate = 1.46 +/- 0.06um
 Mean Flow Pore size of Polystyrene/ePTFE composite = 1.74 +/- 0.08um
 Maximum Pore Size of base laminate = 5.22 +/- 0.65 um
30 Maximum Pore Size of Polystyrene/ePTFE composite = 3.46 +/- 0.22 um

- The above data shows that a porous polystyrene network has been generated within the ePTFE membrane without significantly compromising the properties influenced by the pore size of the base membrane i.e WEP and air flow. Further as shown in Figure 4 incorporation of the microporous
35 polystyrene has increased the diffused reflectance of the membrane. It can be seen from the above data that effective interconnectivity of the membrane is maintained even through the composite membrane pore size is not three times lesser than that of the base membrane.

Example 2

Polystyrene (MW 250,000, Cat# 18,242-7 from Aldrich Chemical Co.) was blended with cyclohexane (Aldrich Chemical Co.) in an Erlenmeyer flask at approximately 60°C till a clear solution of 10 wt. % polymer was obtained.

- 5 The Erlenmeyer flask was transferred to an oven maintained at 60°C. An expanded microporous PTFE laminate (Mean Flow Pore Size 1.7um +/- 0.03 and Maximum Pore Size of 4.56 +/- 0.34), obtained from W. L. Gore & Associates, Inc., was fixed onto a hoop. The hoop with the membrane on it was placed in an oven. The polystyrene solution was poured onto the hoop.
- 10 The membrane was readily wetted by the solution. The entire hoop was then quenched into liquid nitrogen. The membrane was removed from the nitrogen and then dropped into a bath of isopropanol at room temperature to extract the cyclohexane. The membrane was then dried by vacuum to remove the isopropanol, resulting in a co-continuous microporous structure of polystyrene and PTFE (e.g Figure 5 which is an SEM taken at 4.6 kx.).
- 15

Example 3

- A 4 Wt. % of low density polyethylene (MW 125000 Cat # 042 from Scientific Polymer Products Inc.) solution was prepared in diphenyl ether (from Aldrich). The blending was done at approximately 170°C. The solution was forced (using the bottom of an Erlenmeyer flask heated to approximately the same temperature as the polymer solution) by hand into the pores of an expanded microporous PTFE (Mean Flow Pore Size of 3.35 +/- 0.35 um Maximum Pore Size of 10.79 +/- 0.22um) membrane which was restrained in a hoop. The ePTFE membrane in the hoop was also maintained at 150 - 160°C. The membrane (ePTFE + polymer solution) was then quenched into ice water at 1 - 3°C. The diphenyl ether was extracted using acetone (at room temperature). The acetone was then removed by air drying resulting in co-continuous microporous structure of low density polyethylene and PTFE (e.g Figure 6 which is an SEM taken at 3.7 kx.).
- 20
- 25
- 30

WEP of base membrane before gamma radiation: 8 +/- 0.41 psi
(membrane leaks)

WEP of LDPE/ePTFE composite before gamma radiation: 9.67 +/- 1.02 psi (membrane leaks)

- 35 WEP of base membrane after gamma radiation: 5.83 +/- 0.24 psi
(membrane ruptures)

WEP of LDPE/ePTFE composite after gamma radiation : 9 +/- 1.08 psi
(membrane leaks) .

The above data shows that the ePTFE/LDPE composite helps retain the WEP of the membrane after gamma radiation (Radiated to 5Mrads +/- 10%). It is further noted that even prior to radiation the WEP is not significantly compromised due to the incorporation of LDPE.

5

Example 4

A hydrophilic thermoplastic polyurethane (from W.L. Gore & Associates Inc.) was blended with a solvent mixture of dimethyl acetamide (Scientific Polymer Products Inc.) and isopropanol (Aldrich) (55:45 by weight) in an Erlenmeyer flask to make a solution of 5 wt. % polymer. The blending was carried out at 85°C. The solution was then allowed to cool to room temperature (27°C). The solution was forced by hand (as described in Example 3) into the pores of an expanded PTFE (Mean Flow Pore Size of 7.3 +/- 0.82 um, Maximum Pore Size of 64 um) membrane (at room temperature) which was retrained in a hoop. The membrane was then quenched into isopropanol (also at room temperature). The isopropanol was extracted with acetone (Aldrich) and then air dried. The result is a co-continuous microporous structure of polyurethane and PTFE (e.g Figures 7a and 7b). A drop of distilled water when place on the base membrane beaded up. However a drop of distilled water place on the polyurethane / ePTFE composite wetted through the membrane and clarified it. This demonstrates that the wettability of the base ePTFE membrane has been altered by forming the polyurethane / ePTFE composite.

Example 5

A hydrophilic thermoplastic polyurethane (from W.L. Gore & Associates) was blended with a solvent mixture of dimethyl acetamide (Aldrich) and isopropanol (Aldrich) (55:45 by weight) in an Erlenmeyer flask to make a solution of 10 wt. % polymer. The blending was carried out at 85°C. The solution was then allowed to cool to room temperature (27°C). The solution was then forced (as described in Example 3) into the pores (as described in Example 3) of an expanded microporous PTFE (Mean flow pore size of 7.3 +/- 0.82um, Maximum Pore Size of 64 um) membrane (at room temperature) which had been retrained in a hoop. The entire membrane was then quenched into isopropanol (also at room temperature). The isopropanol was extracted with acetone (Aldrich) and the membrane air dried. The result is a co-continuous microporous structure of polyurethane and PTFE (e.g. Figures 8a and 8b).

Example 6

5 A 10 Wt. % polypropylene (from FINA) solution was prepared in diphenyl ether (Aldrich). The blending was done at 180°C. The solution was forced (as described in Example 3) into the pores of an expanded microporous PTFE (mean flow pore size of 7.3 +/- 0.82 um, maximum Pore Size of 64 um) membrane which was restrained in a hoop. The ePTFE membrane in the hoop was also maintained at 160-170°C. The membrane (ePTFE + polymer solution) was then quenched into liquid nitrogen. The diphenyl ether was extracted using acetone (at room temperature). The acetone was then removed by air drying resulting in co-continuous microporous structure of polypropylene and PTFE (e.g. Figure 9).

Example 7

15 A 5 Wt. % solution of high density polyethylene (MW 50000 Cat # 041 from Scientific Polymer Products Inc.) solution was prepared in diphenyl methane (Aldrich). The blending was done at approximately 170°C. The solution was forced (as described in Example 3) into the pores of an expanded microporous PTFE (mean flow pore size of 7.3 +/- 0.82 um, Maximum Pore Size of 64 um) membrane which was restrained in a hoop. The ePTFE membrane in the hoop was also maintained at 150 - 160°C. The membrane (ePTFE + polymer solution) was then quenched into ice water at 1 - 3°C. The diphenyl methane was extracted using acetone (at room temperature). The acetone was then removed by air drying resulting in co-continuous microporous structure of high density polyethylene and PTFE (e.g. Figure 10).

Example 8

30 A 5 Wt. % solution of polyvinylidene fluoride (PVDF) (MW 530000 Cat# 34,707-8 from Aldrich) solution was prepared in a mixture of dimethyl acetamide (Aldrich)(DMAc) and Isopropanol (IPA) in the ratio of 60:40. The blending was carried out at 85°C. The solution was then allowed to cool to room temperature (27°C). The solution was forced into the pores of an expanded microporous PTFE (Mean Flow Pore Size of 3.35 +/- 0.35 um Maximum Pore Size of 10.79 +/- 0.22um) membrane which was restrained in a hoop. The membrane (ePTFE + polymer solution) was then quenched into isopropanol at room temperature. The isopropanol was extracted by washing with acetone. The acetone is subsequently removed by vacuum drying

resulting in a co-continuous microporous structure of PVDF and ePTFE (see Figures 11a and 11b which are SEMs taken at 1.0 kx. and 3.0 kx.).

CLAIMS:

1. A composition consisting essentially of a co-continuous porous combination of a base polymer and a different second polymer:
 - 5 wherein each polymer has a structure consisting of a convoluted matrix which defines convoluted, tortuous, interconnected void paths; wherein said convoluted matrixes of each polymer interpenetrate the void paths of one another; and
 - wherein the void path of said base polymer is microporous.
- 10 2. The composition of Claim 1 where the said paths of the second polymer are also microporous.
3. The composition of Claim 2 wherein the base polymer is selected from the class consisting of polyolefins, polystyrene, fluoropolymers, polyurethanes, polysulfones, polyamides, polyimides, polyacrylics,
 - 15 polyketones, polycarbonates, polyesters, rubbers, and co-polymers and blends thereof.
4. The composition of Claim 3 wherein the second polymer is selected from the class consisting of polyolefins, polystyrene, fluoropolymers, polyurethanes, polysulfones, polyamides, polyimides, polyacrylics,
 - 20 polyketones, polycarbonates, polyesters, rubbers, and co-polymers and blends thereof
5. The composition of Claim 4 wherein the base polymer is a fluoropolymer.
6. The composition of Claim 5 wherein the fluoropolymer is polytetrafluoroethylene.
- 25 7. The composition of Claim 6 wherein the second polymer is polystyrene.
8. The composition of Claim 6 wherein the second polymer is a polyolefin.
9. The composition of claim 6 wherein the second polymer is a polyurethane.
10. The composition of Claim 6 wherein the second polymer is polyvinylidene fluoride.
 - 30
11. Process for preparing a co-continuous porous combination of a base polymer and a second polymer which comprises:
 - (a) filling the pores of a microporous organic polymer with a solution of a second different organic polymer;
 - 35 (b) causing the solution of the second polymer to phase separate while in the pores of the microporous polymer into a polymer rich phase and a solvent rich phase;

- (c) extracting the solvent rich phase from the pores of the microporous polymer;
- (d) drying the material of step (c).

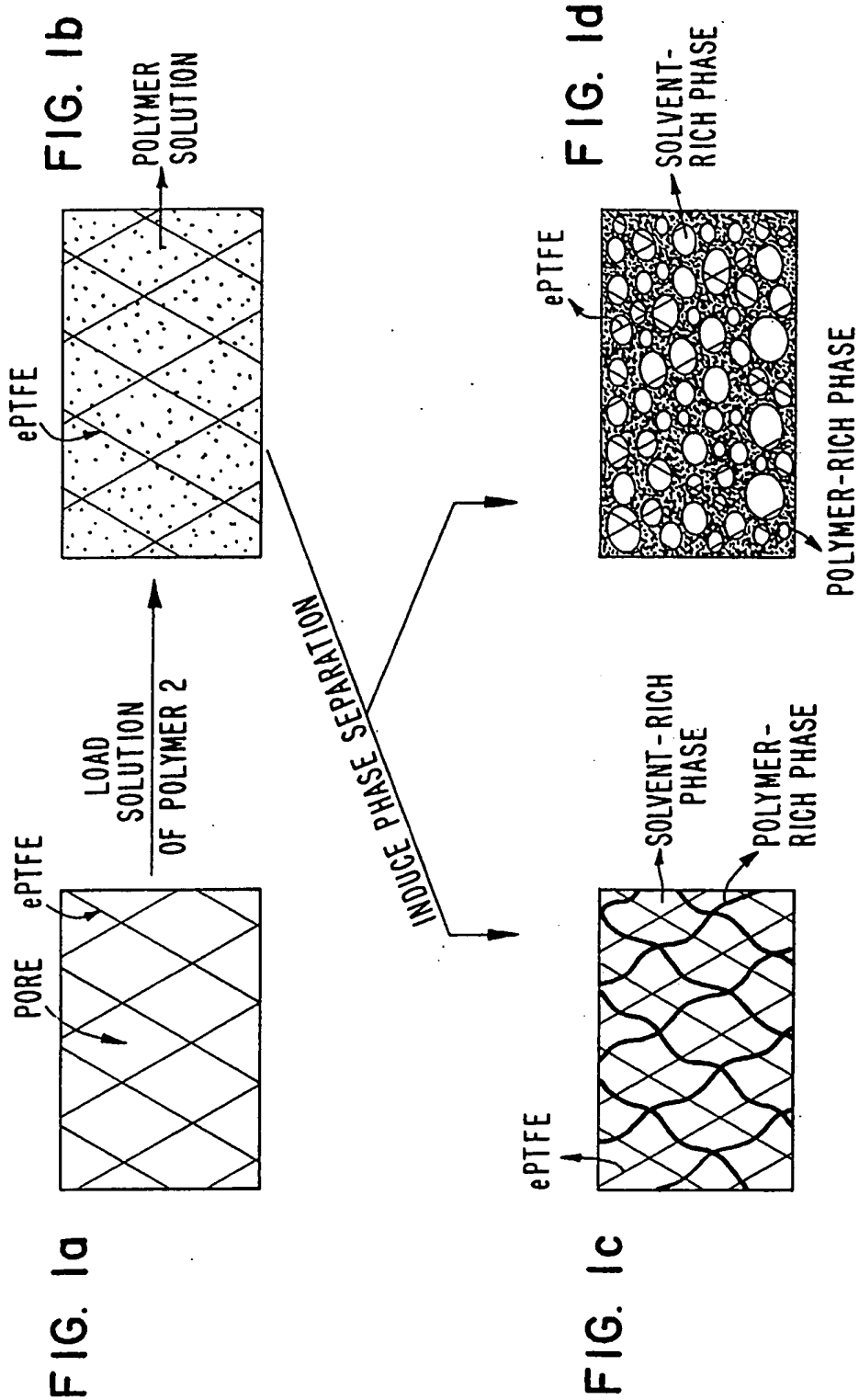


FIG. 2a

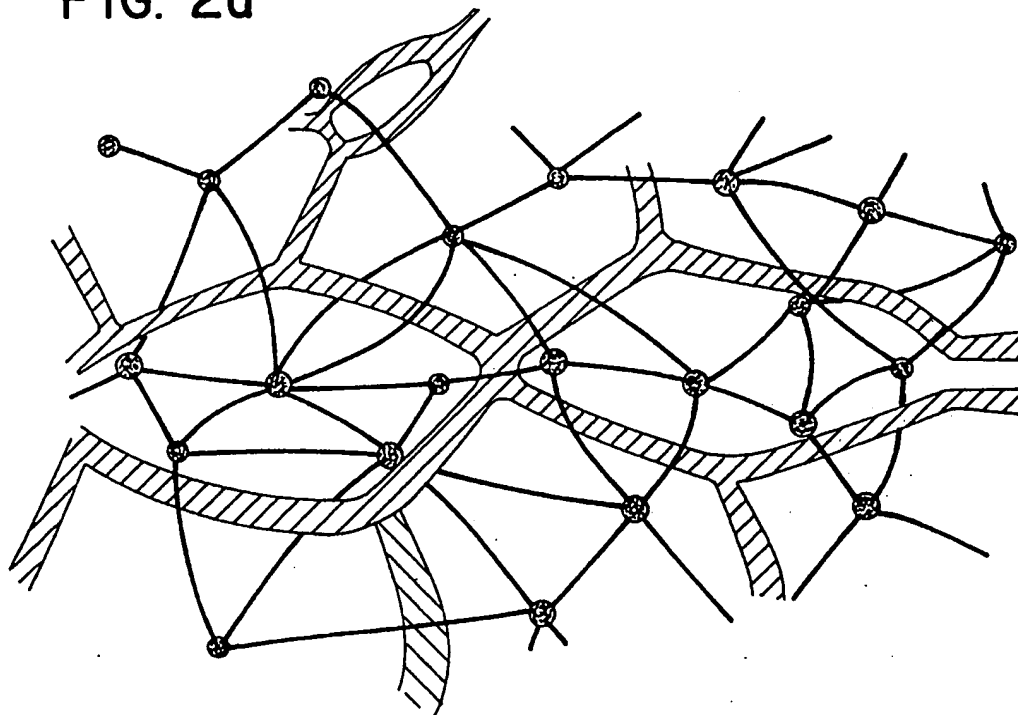
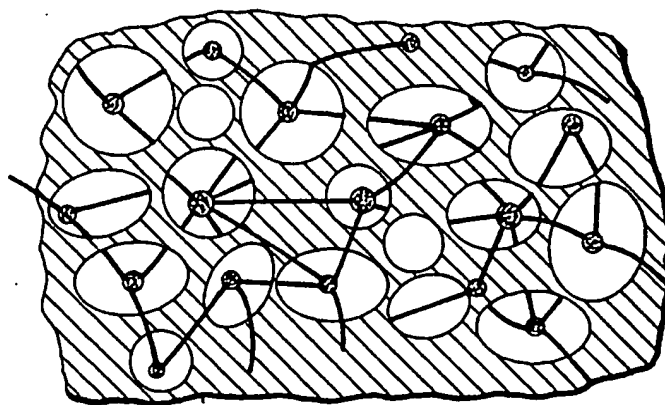


FIG. 2b



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FIG. 3a

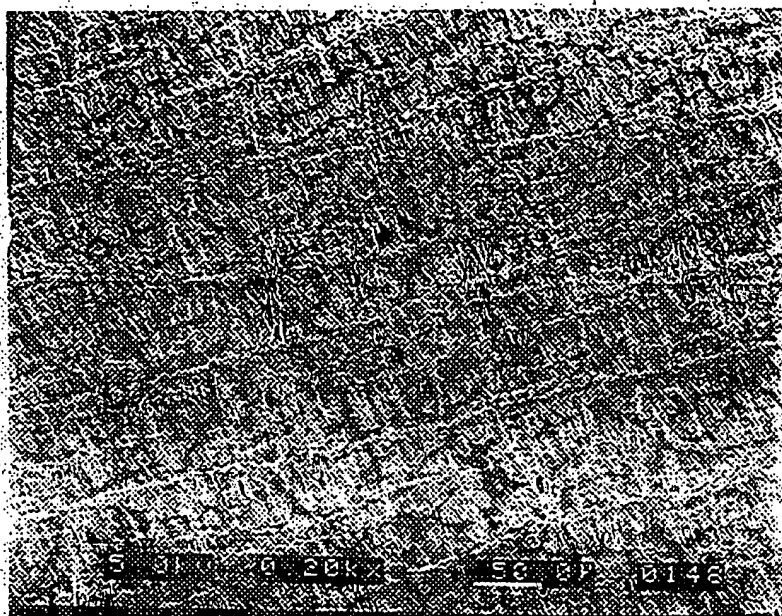
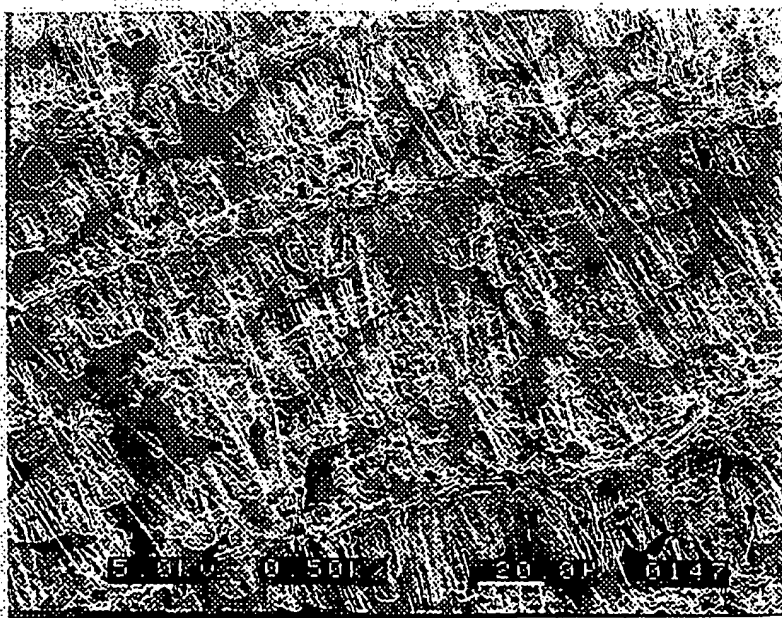
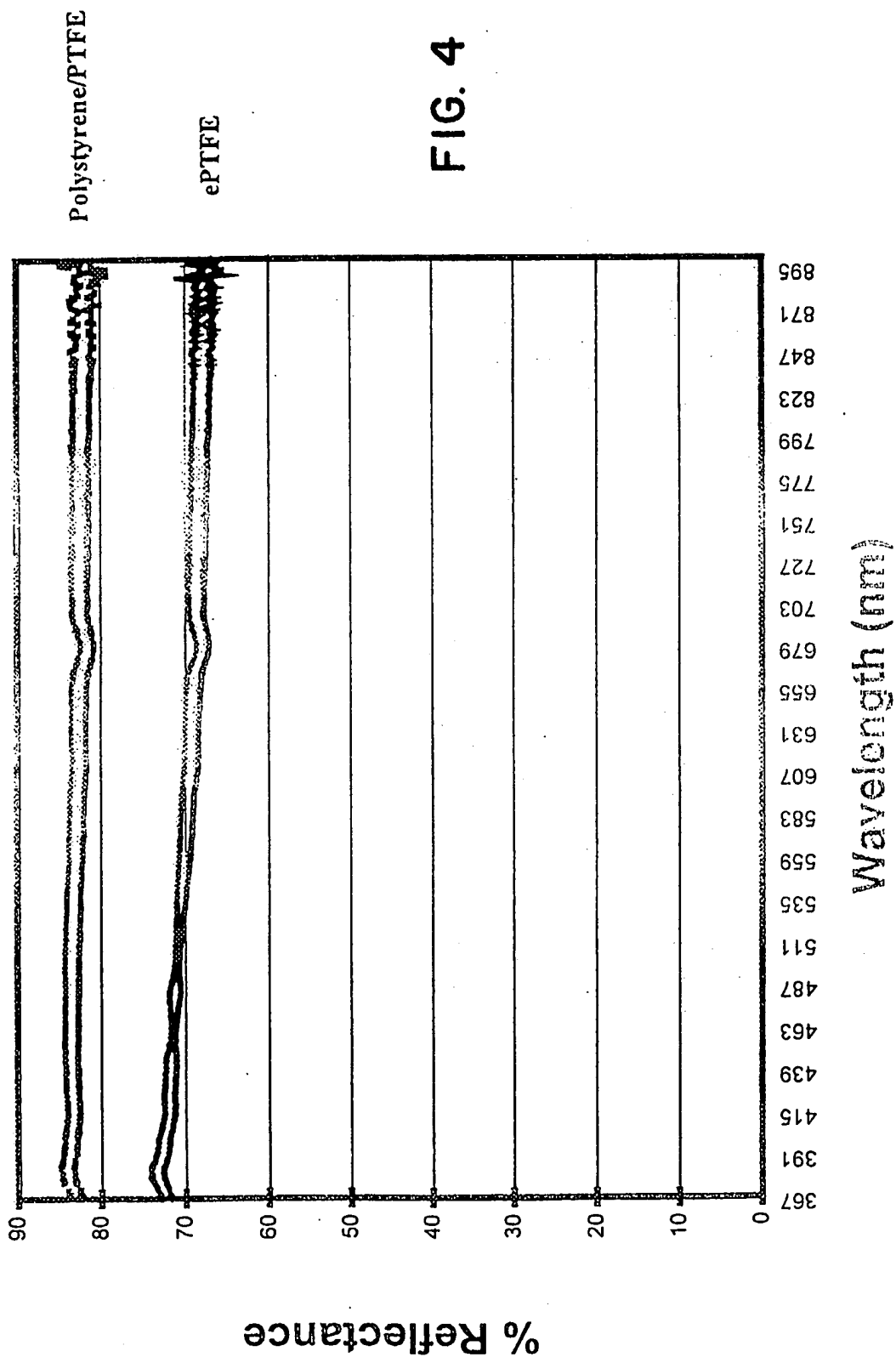


FIG. 3b



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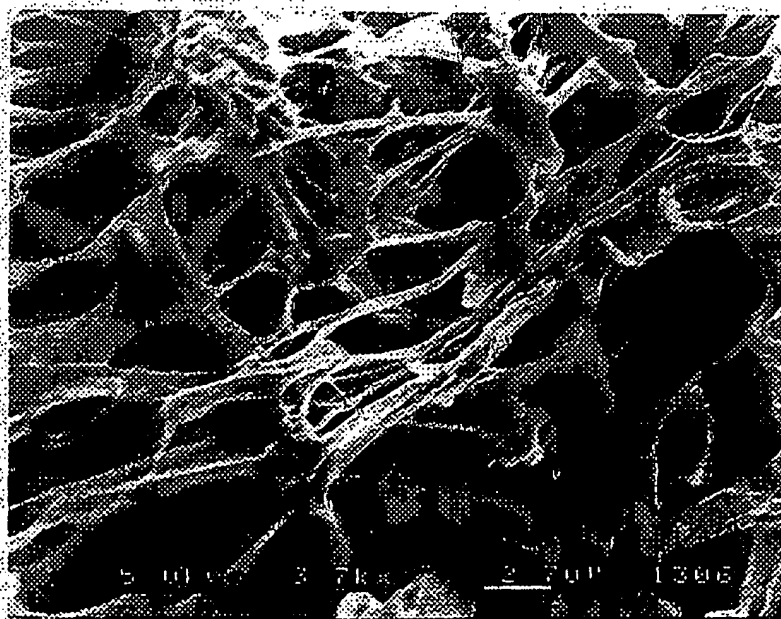


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FIG. 5



FIG. 6



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FIG. 7a

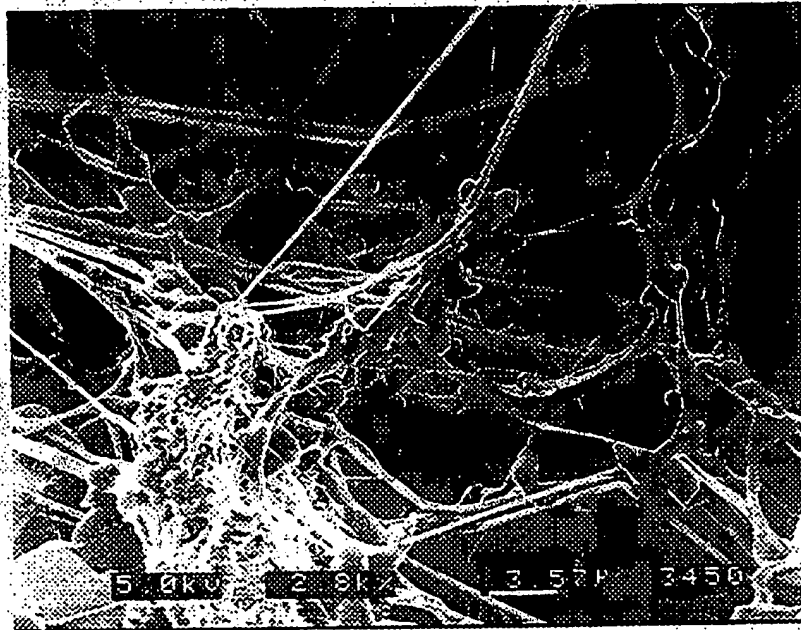
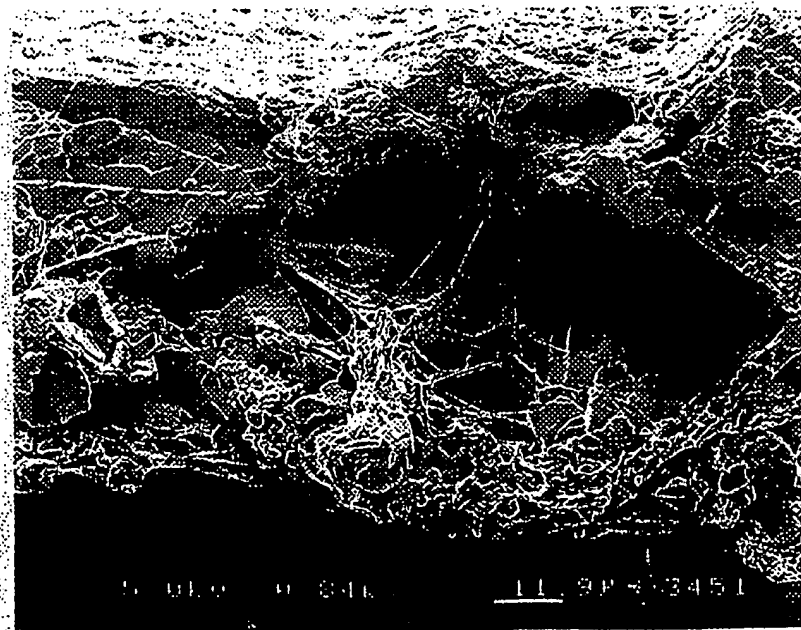


FIG. 7b



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FIG. 8a

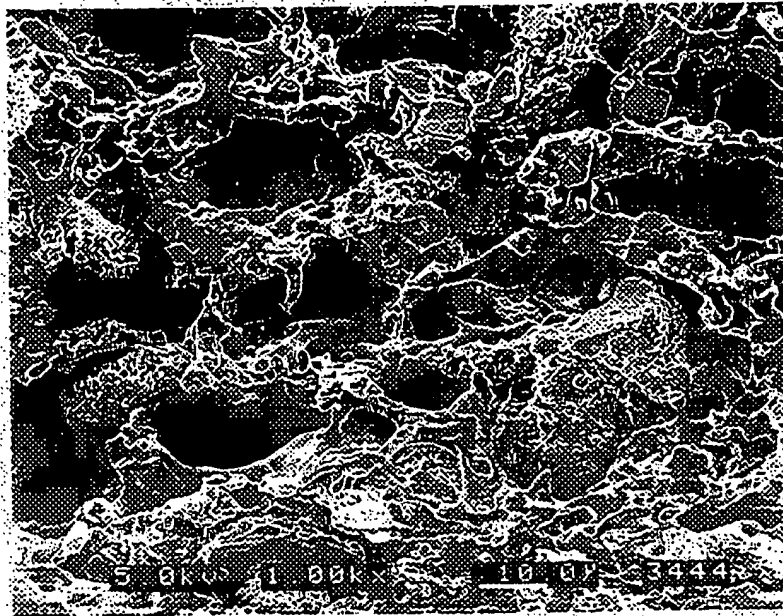


FIG. 8b



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FIG. 9

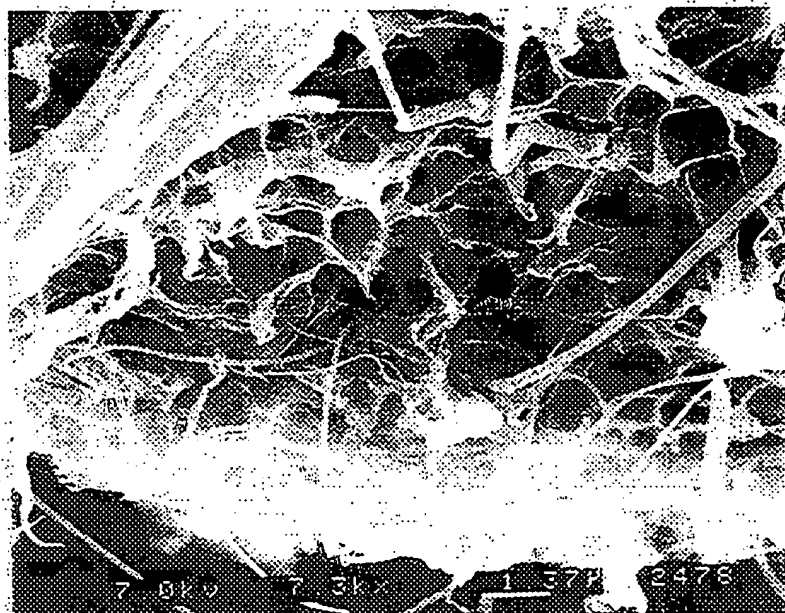


FIG. 10

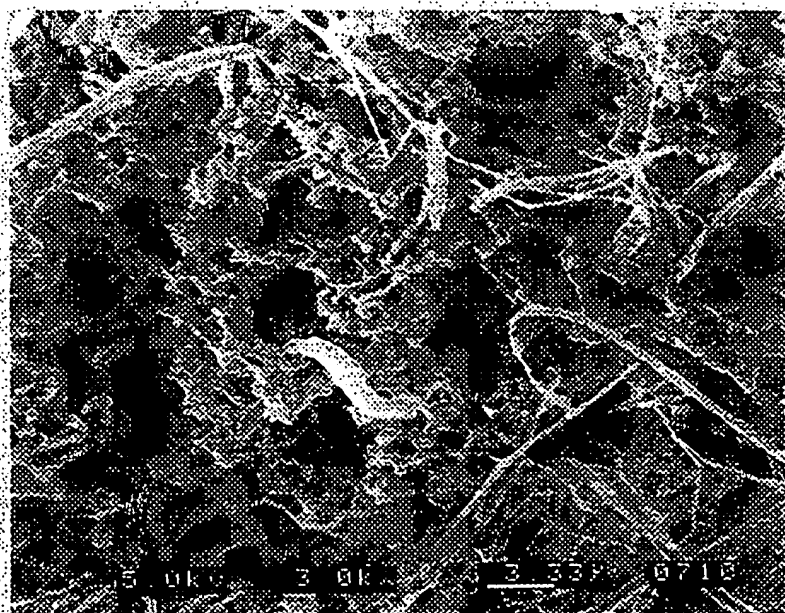


FIG. 11a

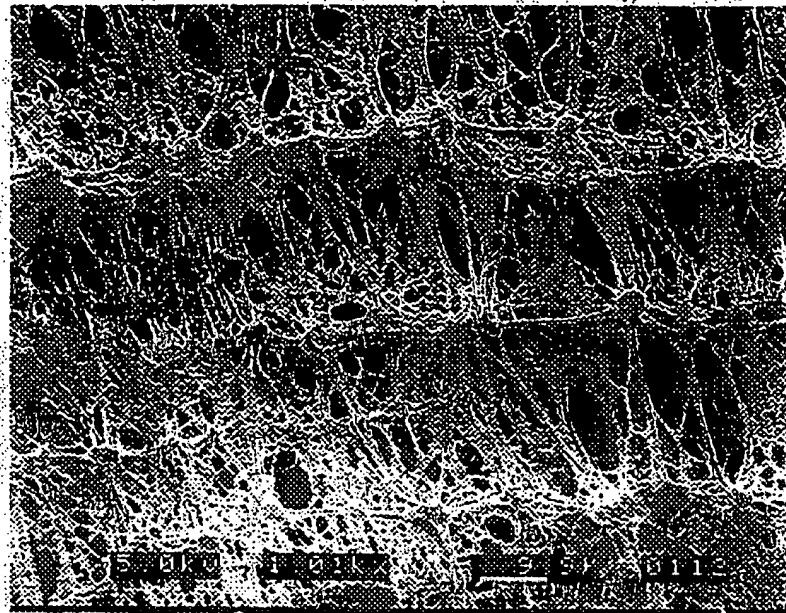
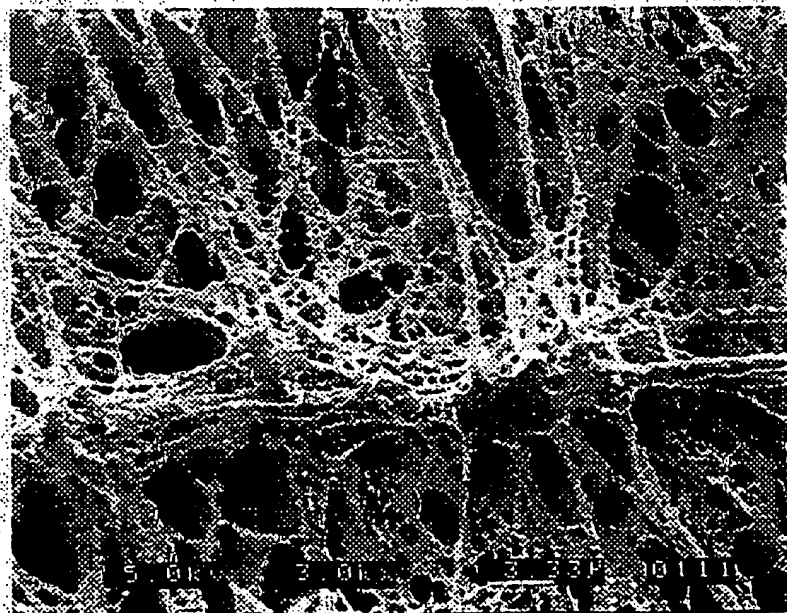


FIG. 11b



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/06323

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J9/42 B01D69/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 113 912 A (K. OKITA) 12 September 1978 see column 8, line 26-40; claims ---	1-10
X	PATENT ABSTRACTS OF JAPAN vol. 12, no. 263 (C-514), 22 July 1988 & JP 63 046240 A (KANEBO LTD), 27 February 1988, see abstract ---	1-10
A	US 4 761 232 A (D.G. BRIGHT) 2 August 1988 cited in the application see claims ---	1
A	US 5 277 915 A (R.B. PROVONCHEE, E.A.) 11 January 1994 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

12 August 1997

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

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